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Project ID: **BAT309**

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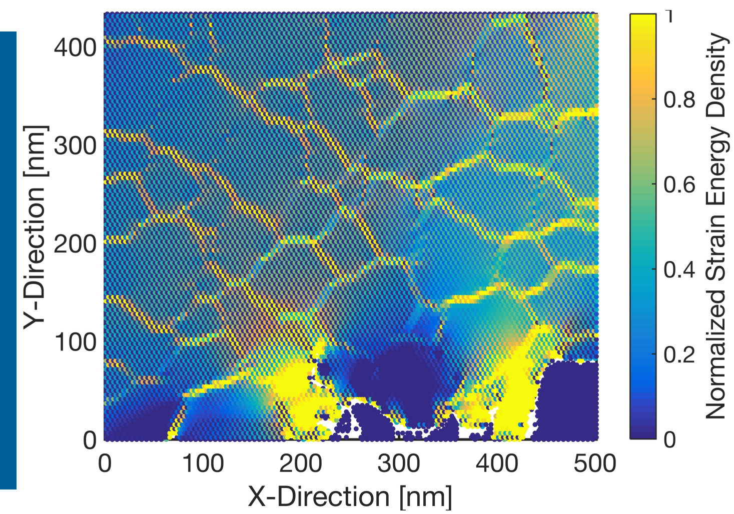
ELECTRODE MATERIALS DESIGN AND FAILURE PREDICTION



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Date: June 3rd 2020
Location: Arlington, VA

OVERVIEW

Timeline

- Project start date: October 2019
- Project end date: September 2022
- Percent complete: 25%

Barriers

Barriers addressed

- Dendrite growth in solid state electrolytes
- Delamination induced performance decay in cathode/solid-electrolyte interface.

Budget

- $500k/year
  - 0.55 FTE Staff Scientist
  - 1.5 FTE Postdoc
  - 0.5 FTE Graduate Student

Partners

- Kenneth Higa (LBNL)
- Anh Ngo/Larry Curtiss (ANL)
- Nitash Balsara (LBNL)
- Shrayesh Patel (U. of Chicago)
- Jurgen Janek (U. of Giessen)

RELEVANCE

Objectives:

- Investigate the lithium dendrite growth mechanism in solid electrolytes
  - Heterogeneous lithium deposition and dendrite growth
  - Mechanical properties of the materials and chemo-mechanical interactions.

- Elucidation of the degradation mechanism at the solid-electrolyte/cathode interface
  - Volume change and stress evolution in solid-electrolyte/cathode composite
  - Delamination between solid-electrolyte and cathode and its link to capacity fade during cycling

MILESTONES

- Elucidate the difference in delamination mechanisms for NMC/LLZO- and LCO/LLZO- type cathode/SEIs. (December, 2019).

Completed

- *Go/No-Go Decision*: Investigate impact of exchange current density on delamination-induced capacity fade. If effect is minor, use experimentally observed exchange current values. Otherwise, use value obtained from DFT calculations. (March, 2020).

Completed

- Develop continuum model for charge transport and mechanical degradation incorporating an interphase layer between LLZO electrolyte and NMC cathode. (June, 2020).

In progress

- Gain understanding of growth rate of electrodepositing lithium nuclei. (September, 2020).

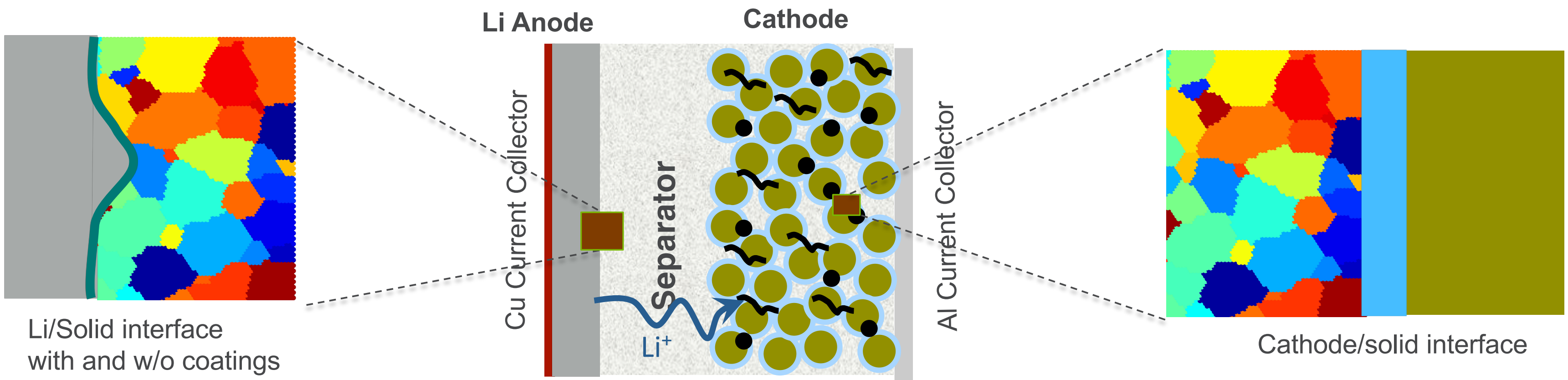
In progress

Sept 2019 | Dec 2019 | March 2020 | June 2020 | Sept 2020

APPROACH

Physics
(Literature: visualization)

Model parameters
(Literature and inhouse: lower length scale theory, experiments)

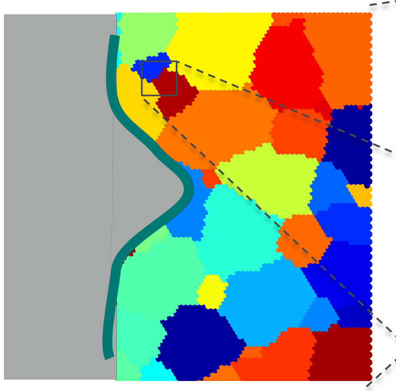


Mathematical modeling at the meso/macro scale (electrochemistry, transport, mechanics)

Material properties
- Dendrite prevention
- Accommodating volume change

Improve understanding
- Grain boundaries
- Chemo-mechanics at interface

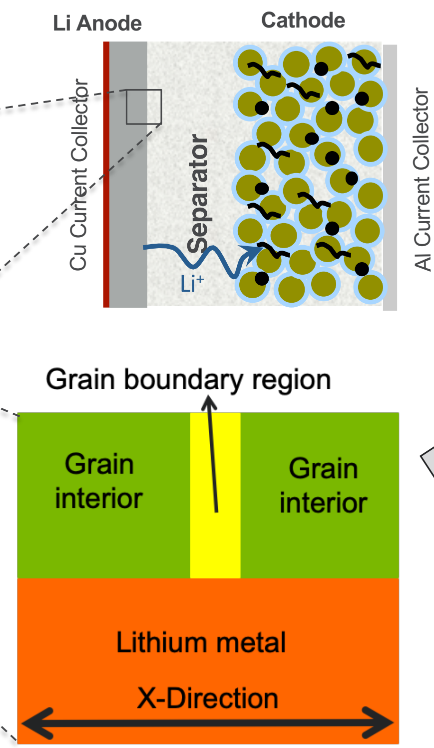
ELASTICALLY SOFT GRAIN BOUNDARIES: LOCATION FOR CURRENT FOCUSING

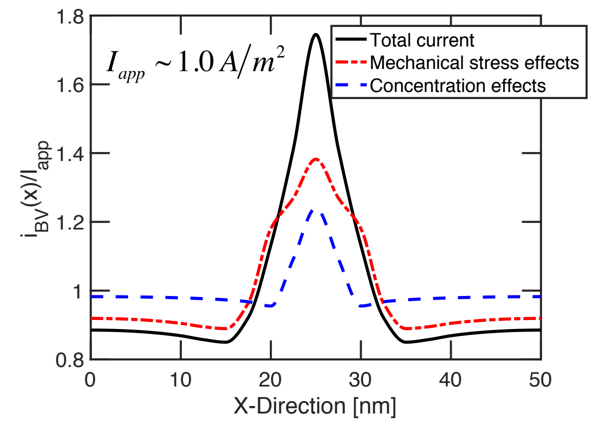


Lithium/solid interface:

i. Li inhomogeneity;

ii. Electrolyte inhomogeneity





$$i_{BV}(x) = i_{BV}\left(\Delta\mu_{e^-}(x), c_{Li^+}(x)\right)$$

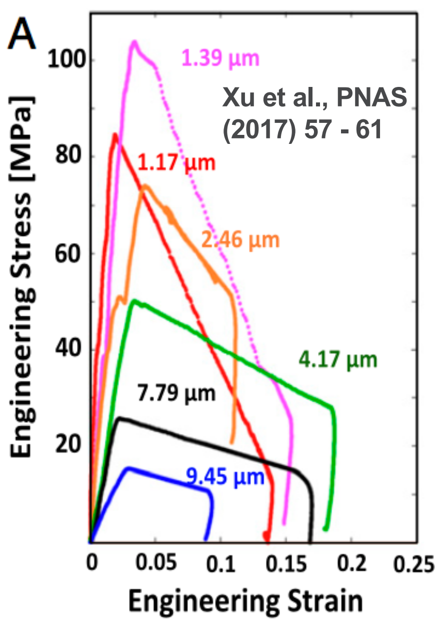
Mechanical stress effect **Concentration effect**

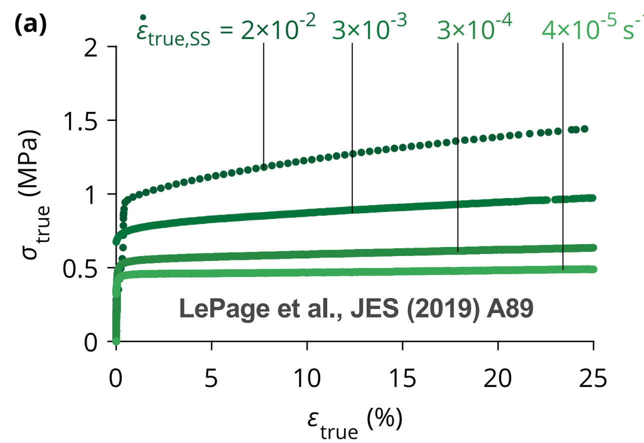
Reaction current density affected by mechanical stress, as well as, concentration differences.

Any inhomogeneities (defects, composite electrolyte) in the electrolyte leads to current focusing

LI YIELD STRENGTH DEPENDS ON RATE OF DEPOSITION AND SIZE OF PROTRUSIONS

Recent experiments have revealed that the yield strength of lithium depends on the rate of deformation, or rate of deposition, as well as size of deposits.





Lithium yield strength increases with increasing rate of deposition

Other numbers of lithium yield strength reported by scientists:

Campbell et al. Sci. Rep. (2018) 2514

$$\sigma_{0,Li} = 30MPa$$

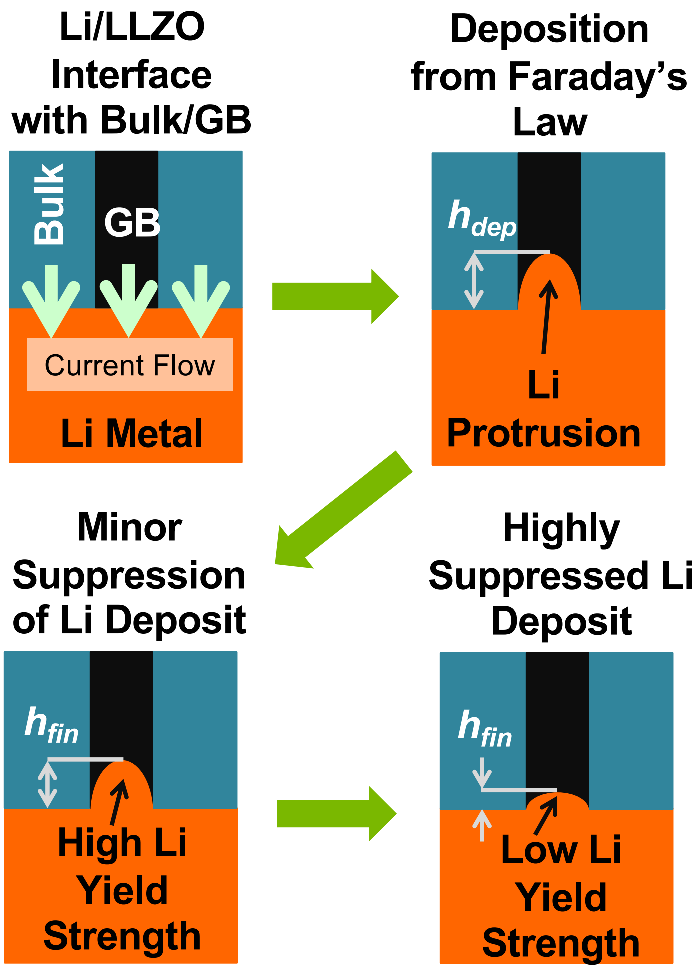
Under compression:
Bulk Li yield strength → **0.81MPa**
(Masias et al., J. Mater Sci. (2019) 2585)

Zhang et al. Cell Reports Physical Science (2020) 1 100012

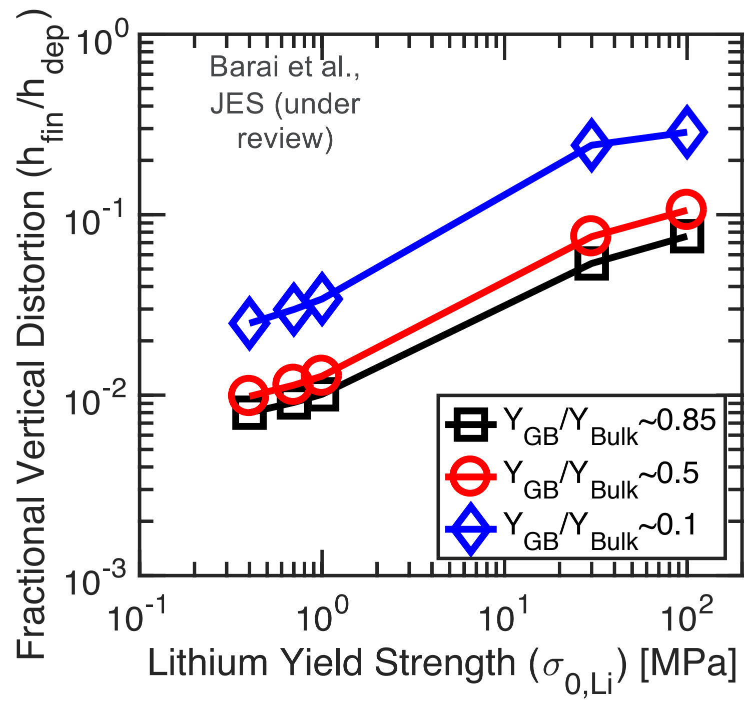
$$\sigma_{0,Li} = 16MPa$$

What are the implications of yield strength on dendrite growth through LLZO solid state electrolytes?

MODELS SUGGEST THAT LI WILL PENETRATE THE GRAIN BOUNDARY



$$\begin{bmatrix} Fractional \\ vertical \\ distortion \end{bmatrix} = \frac{h_{final}}{h_{dep.}}$$



Will the dendrite penetration lead to cracking?

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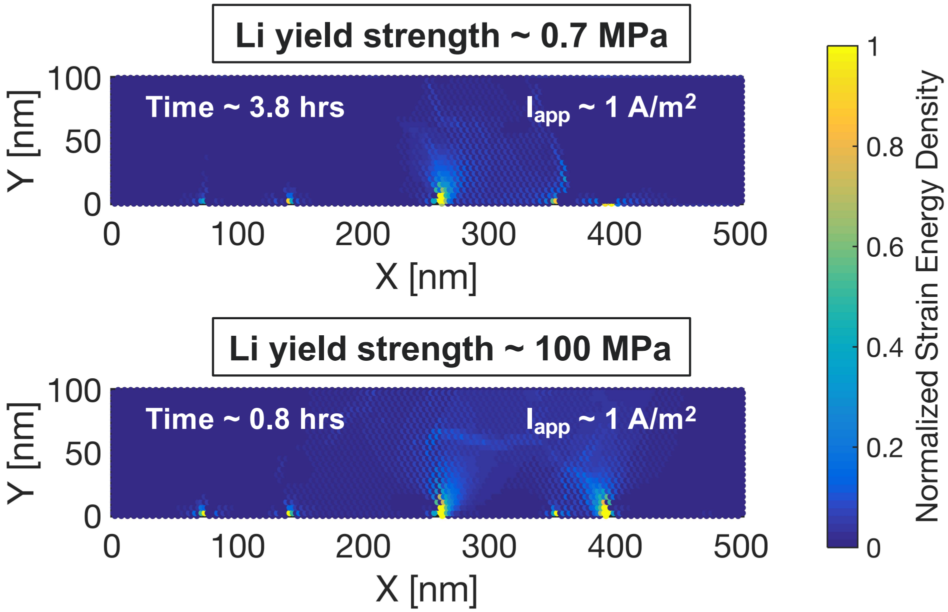
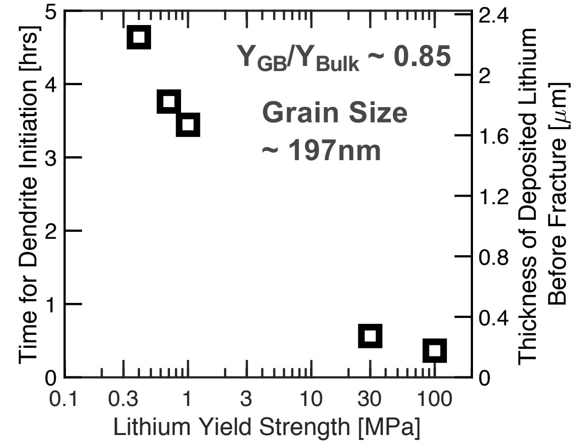
MODEL SUGGESTS THAT FRACTURE POSSIBLE DEPENDING ON DEPOSITION TIME



Impact of Li yield strength

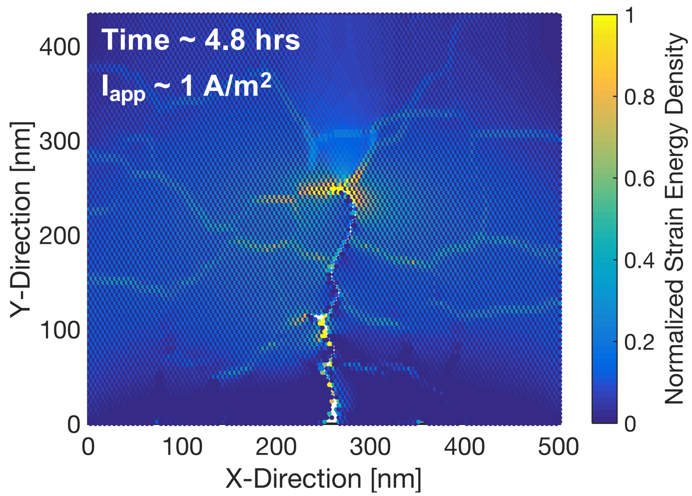


Increasing lithium yield strength results in a decrease in dendrite initiation time, because lithium with higher yield limit behaves as a stronger material.

Lithium yield strength changes the time for dendrite initiation. However, models suggest that cracking occurs when enough Li is deposited

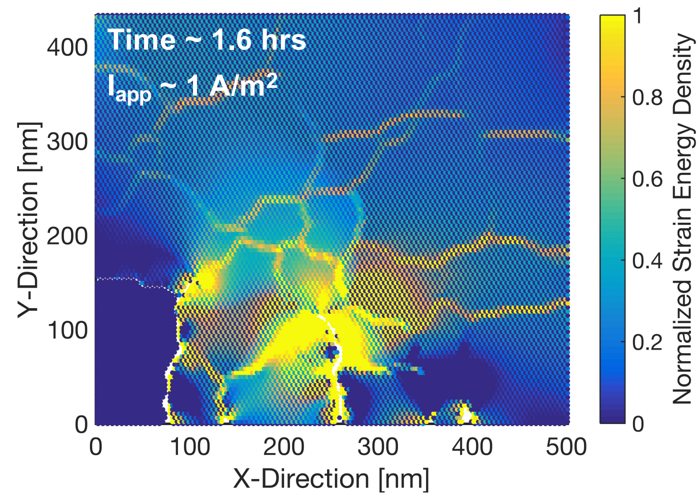
MODEL ALSO SUGGESTS THAT CRACK WILL PROPAGATE INTO CERAMIC

Li yield strength ~ 0.7 MPa



With smaller Li yield strength, the evolution of strain energy is very concentrated at the dendrite tip.

Li yield strength ~ 100 MPa

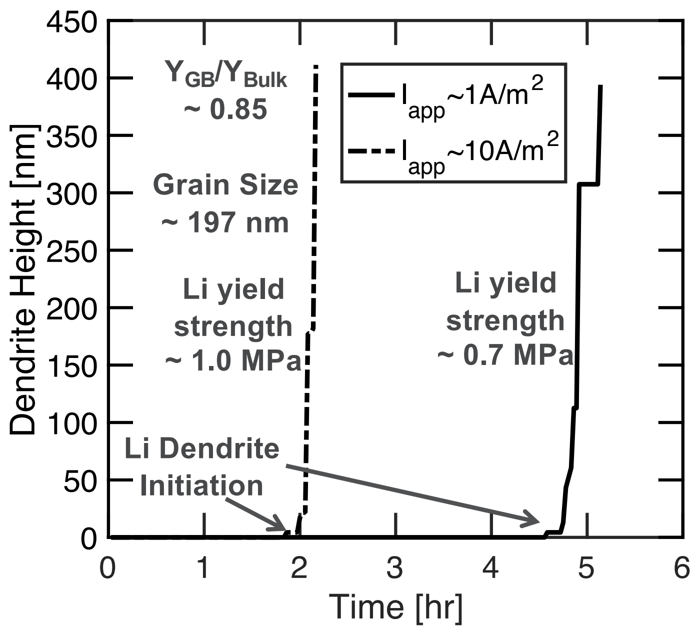


For higher Li yield strength, the evolution of strain energy is distributed all throughout the solid electrolyte domain.

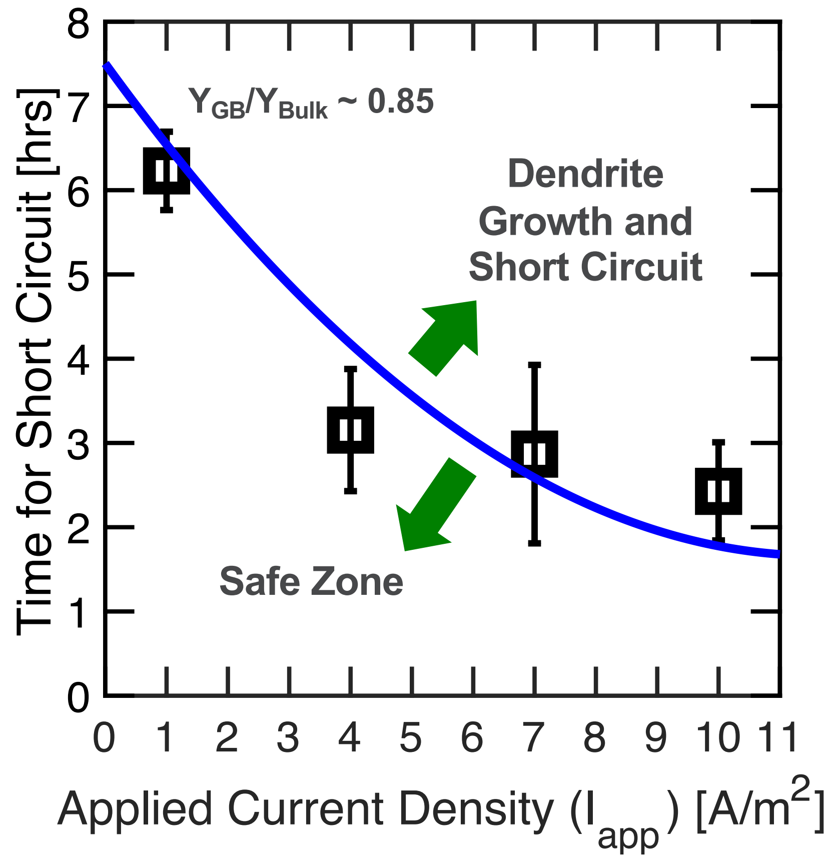
Variation is strain energy distribution with different lithium yield strength leads to needle like dendrites for softer Li and branched dendrites for Li with high yield strength.

WILL CRACKING LEAD TO CELL SHORTING?

Due to viscoplasticity of lithium metal, rate of deposition affects its yield strength.

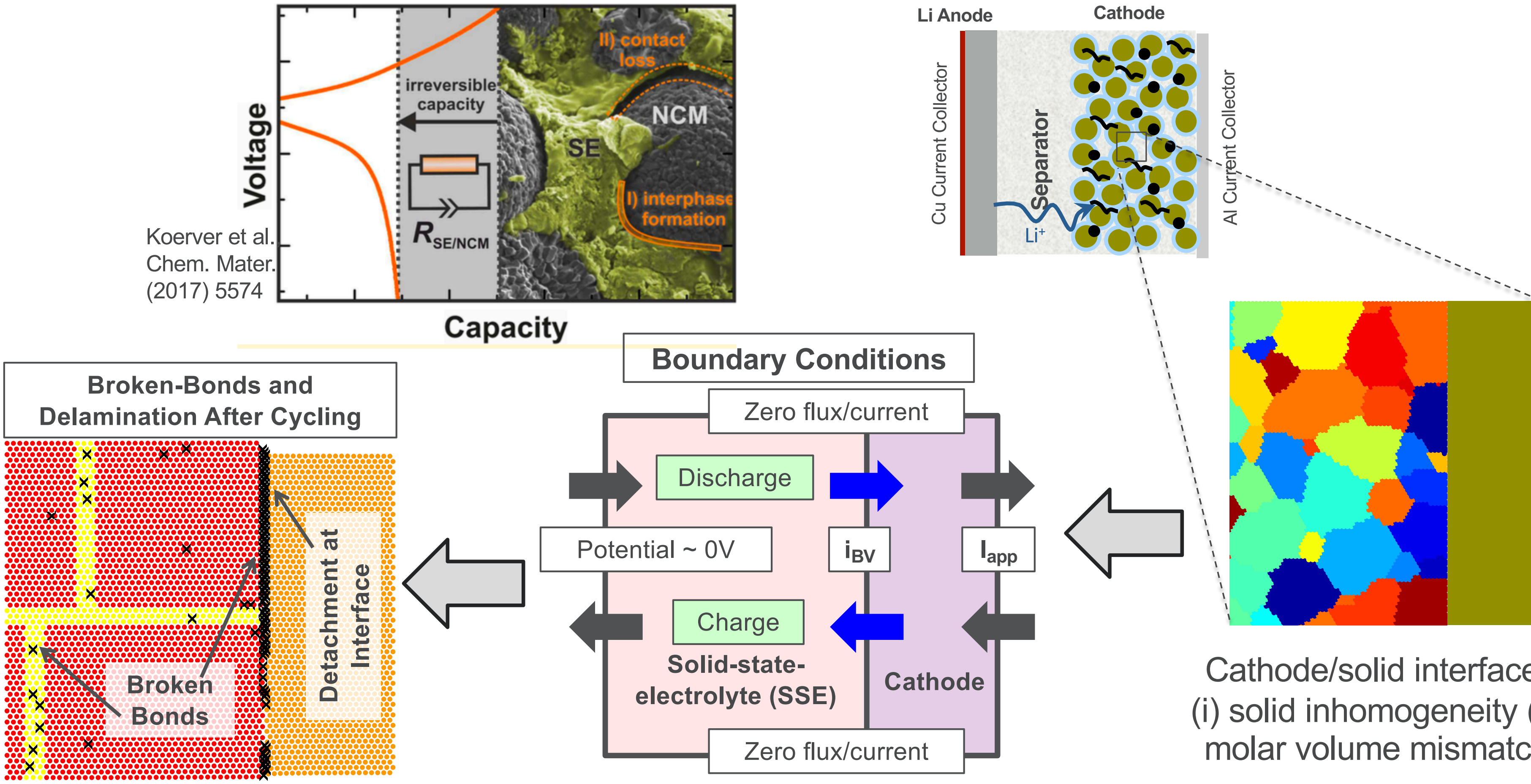


Lithium deposition at higher currents lead to early dendrite nucleation and faster propagation.



Depending on applied current density and time for lithium deposition, it is possible to estimate whether it is safe or dendrites can short the cell.

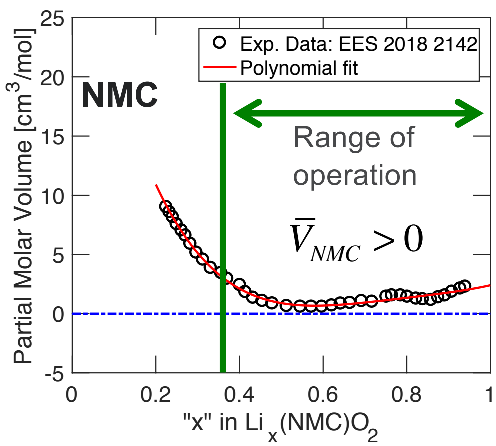
VOLUME CHANGE WITHIN CATHODES LEAD TO DELAMINATION AT THE INTERFACE

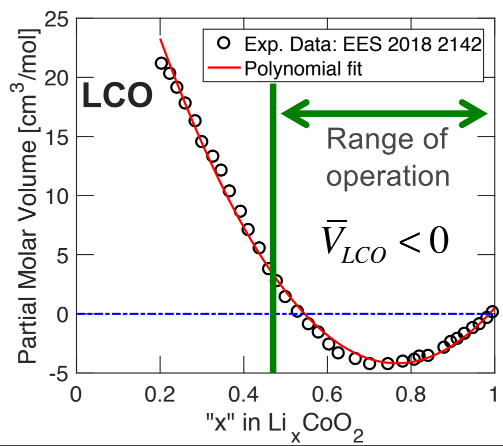


Koerver et al. Chem. Mater. (2017) 5574

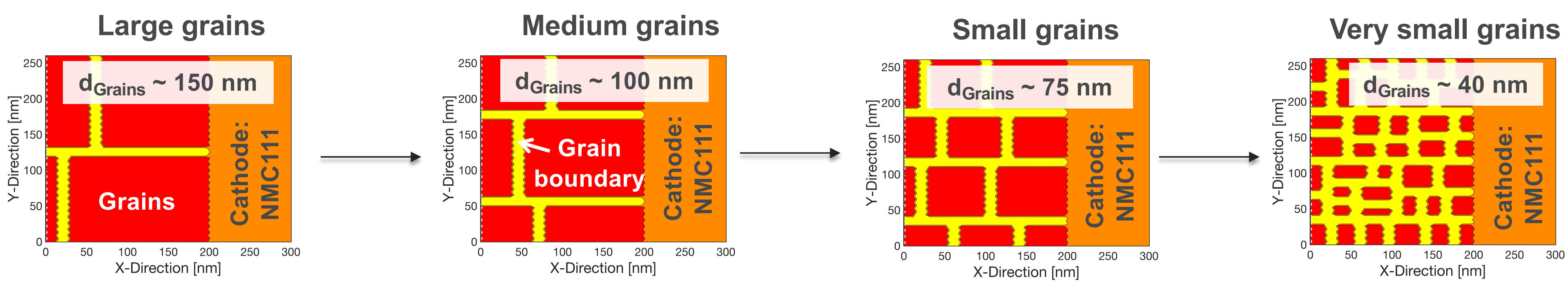
Cathode/solid interface: (i) solid inhomogeneity (ii) molar volume mismatch

PARTIAL MOLAR VOLUME OF LITHIUM LEADS TO DELAMINATION DURING OPERATION





NMC and LCO cathodes demonstrate positive and negative partial molar volume, respectively.



Impact of LLZO grain size on extent of delamination have been investigated.

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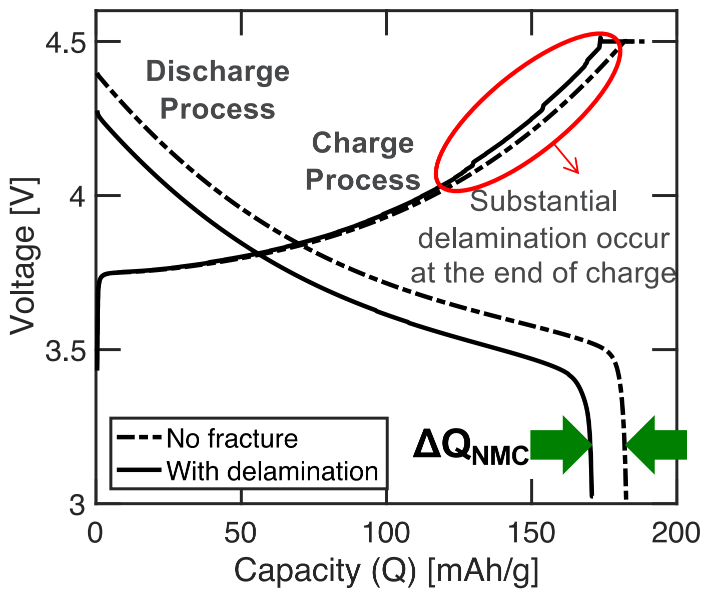
INTERFACIAL DETACHMENT WITHIN NMC AND LCO CATHODES LEADS TO CAPACITY FADE

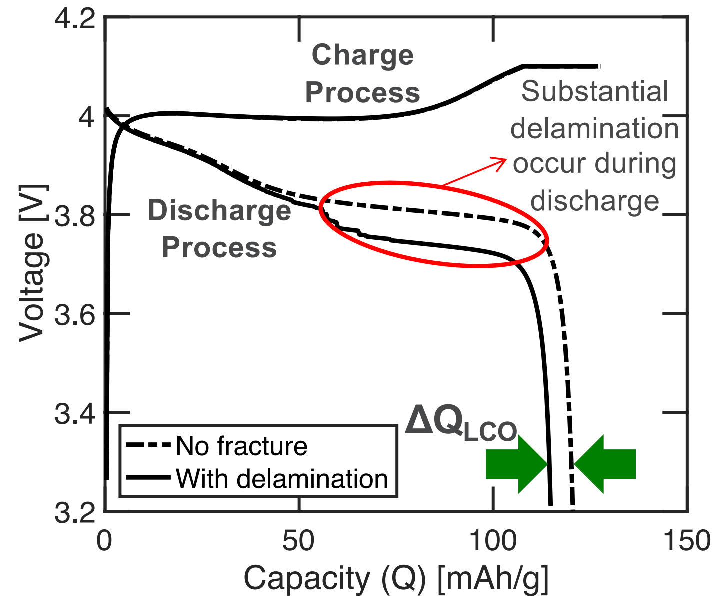
NMC: Voltage window: 3.0V – 4.5V



I_{app} = 1A/m^2

CC-CV Charge and CC Discharge

LCO: Voltage window: 3.2V – 4.1V



Due to the difference in partial molar volume of Li within NMC and LCO, NMC experiences delamination during charge, whereas, LCO experience delamination during discharge.

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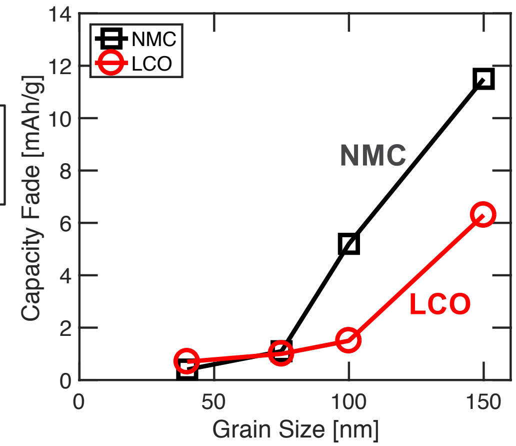
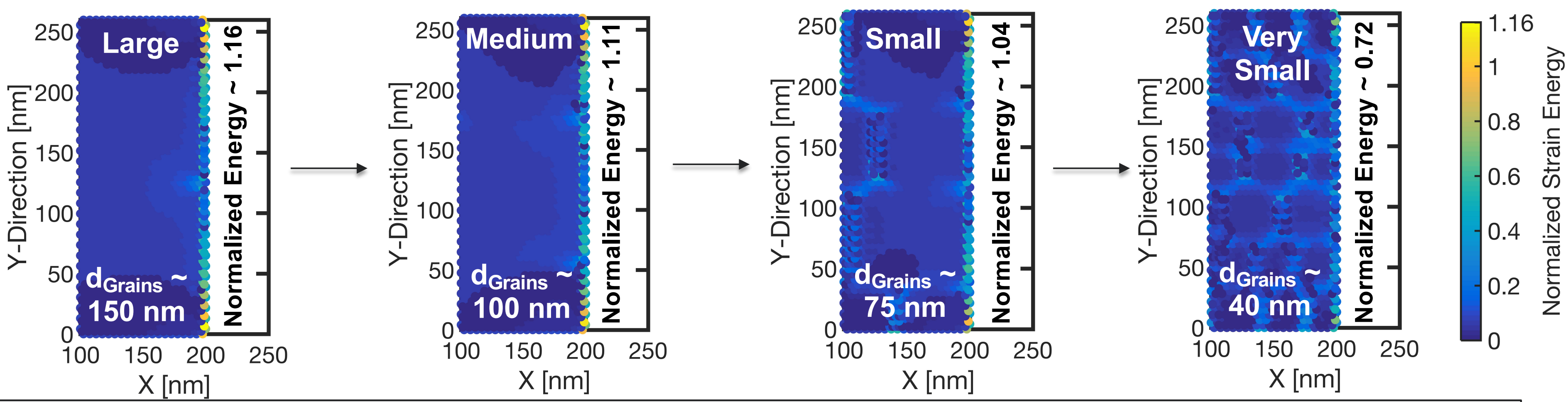
LLZO GRAIN SIZE IMPACTS INTERFACIAL DELAMINATION

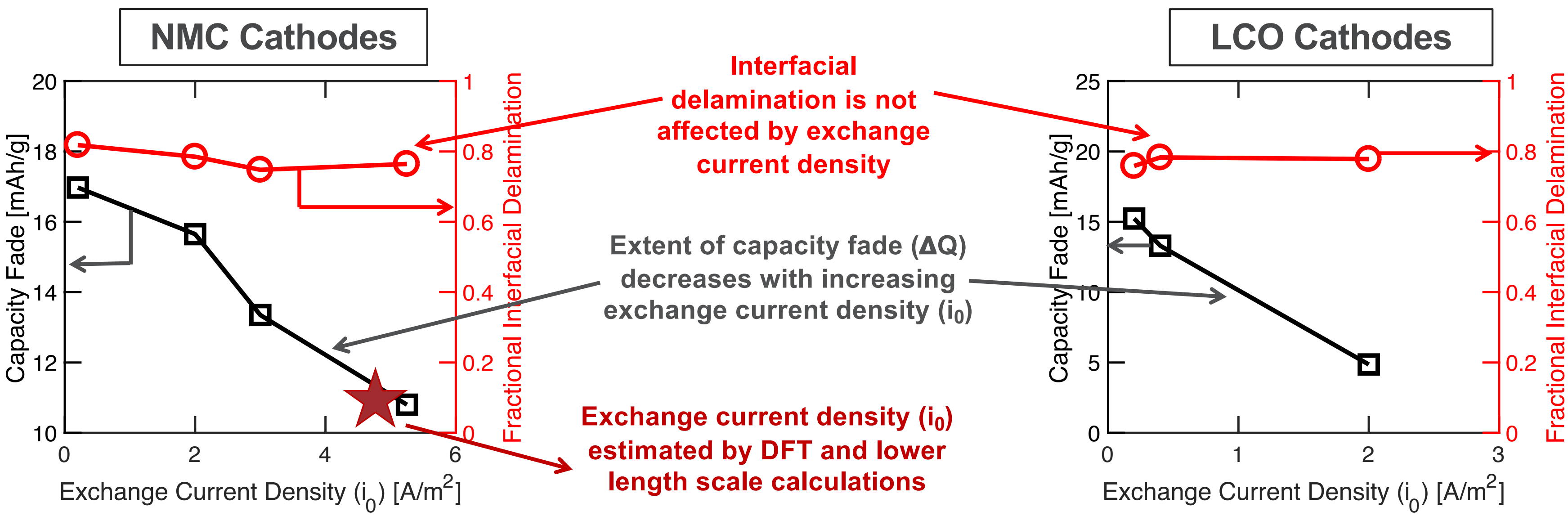
Decreasing grain size helps to minimize the delamination induced capacity fade





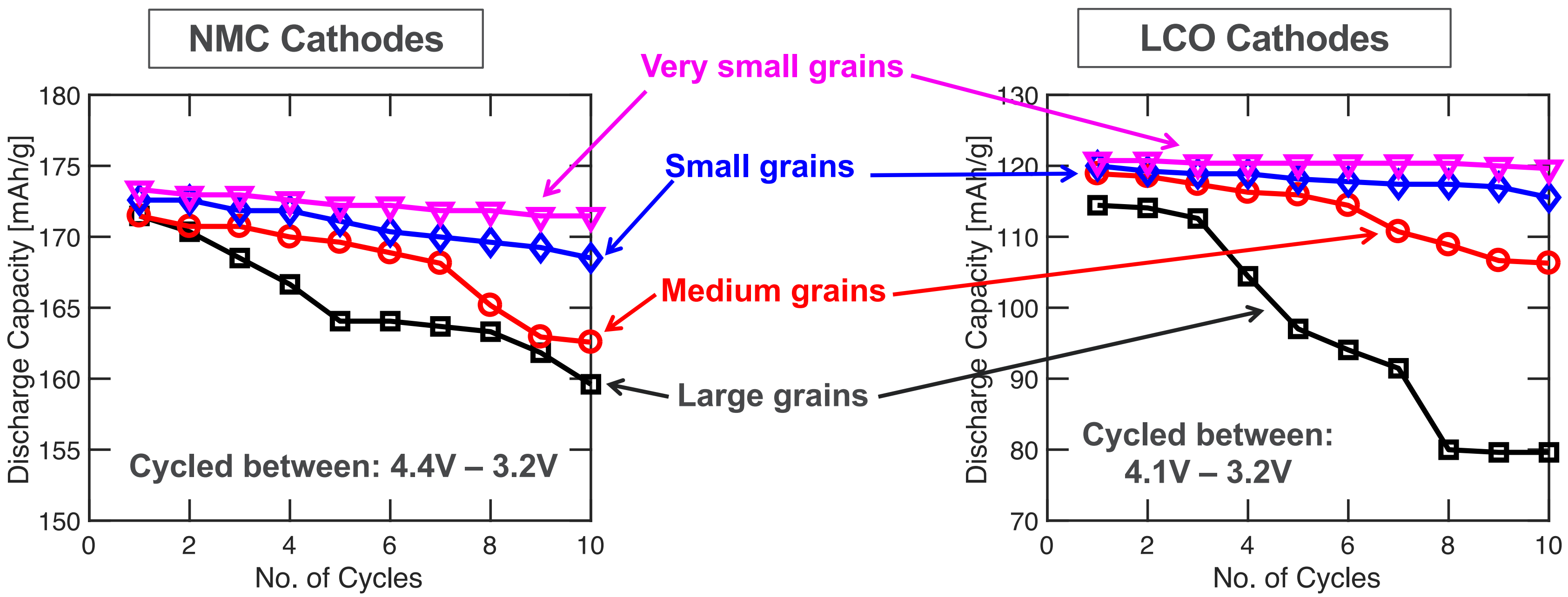
Evolution of less stress in smaller grains lead to decrease in delamination induced capacity fade

EXCHANGE CURRENT DENSITY IS AN IMPORTANT FACTOR



- For both NMC and LCO cathodes, exchange current density does not affect the extent of interfacial delamination.
- However, increasing exchange current density leads to decrease in capacity fade even with the same amount of interfacial delamination, because larger exchange current helps to minimize the interfacial polarization.
- Measurements are needed to accurately estimate this property.

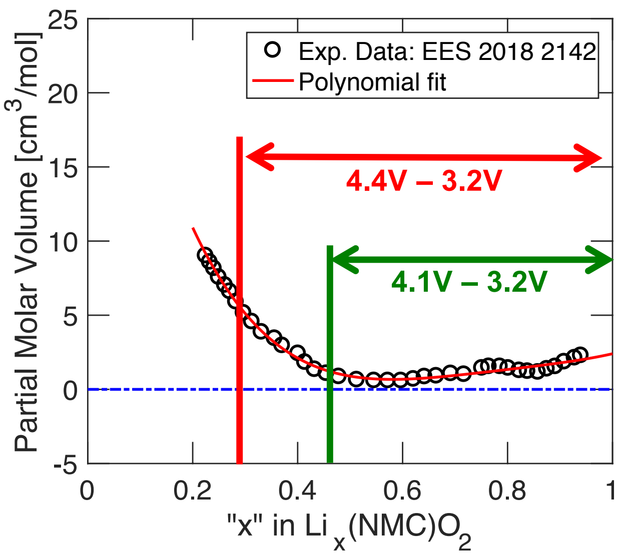
IMPACT OF MULTIPLE CYCLES ON DELAMINATION INDUCED CAPACITY FADE

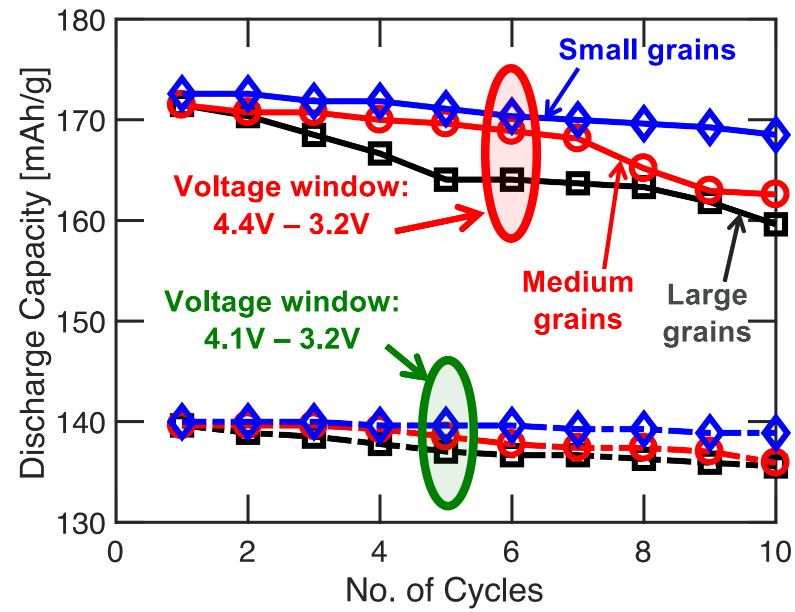


- **Long term cycling demonstrates continuous delamination induced capacity fade for both NMC and LCO cathodes.**
- **Decreasing grain size helps to minimize the delamination induced capacity fade.**

DECREASING POTENTIAL WINDOW OF OPERATION TO MINIMIZE CAPACITY FADE

Minimizing potential window of operation to reduce capacity fade in NMC.





- **While cycling NMC cathodes, minimizing the upper cutoff voltage from 4.4V to 4.1V helps to avoid a certain portion where the partial molar volume of Li within NMC increases substantially.**
- **Decreasing potential window of operation helps to minimize the rate of capacity fade from 1 mAh/g/cycle to 0.2 mAh/g/cycle, which is 5 times improvement.**

RESPONSE TO PREVIOUS YEAR REVIEWER'S COMMENTS

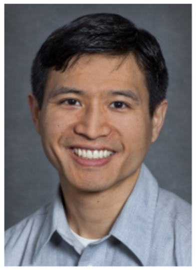
- All the reviewers appreciated the broad approach adopted in this research where interfacial issues of solid state electrolytes with both lithium metal anode, as well as, cathodes have been addressed.

- The reviewers raised concern about the extremely localized nature of the model being developed, where growth of only one dendrite is analyzed.
  - ❖ In response, this year propagation of multiple lithium dendrites through LLZO solid state electrolytes have been addressed. Multiple protrusions nucleate at the hot spots, which are grain-boundaries in the present context. Depending on its ease of growth, only one dendrite propagates.

- The reviewers pointed out the importance of adding solid electrolyte interphases, and cathode electrolyte interphases, in between the electrode and the electrolyte.
  - ❖ In response, the authors have taken up new modeling approaches where interdiffusion of ions, and existence of interphase layers, can be captured.

- The reviewers also pointed out the lack of experimental inputs for proper validation of the model.
  - ❖ In response, the authors have started collaboration with Prof. Jurgen Janek (Justus-Liebig-Universität, Giessen, Germany), who has well established techniques for conducting model experiments.

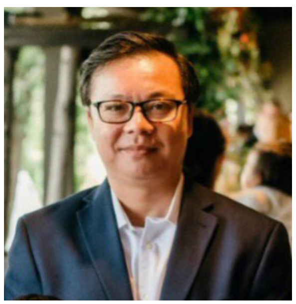
COLLABORATION AND COORDINATION



Kenneth Higa
(LBNL)

Nitash Balsara
(LBNL)

Shrayesh Patel
(U. of Chicago)



Anh T. Ngo/Larry Curtiss (ANL)
Project ID: BAT424

Jurgen Janek (Justus-Liebig-Universität Giessen)

- DOE User Facility
  - Advanced Light Source (ALS), located in LBNL
  - Advanced Photon Source (APS), located in ANL

REMAINING CHALLENGES AND BARRIERS

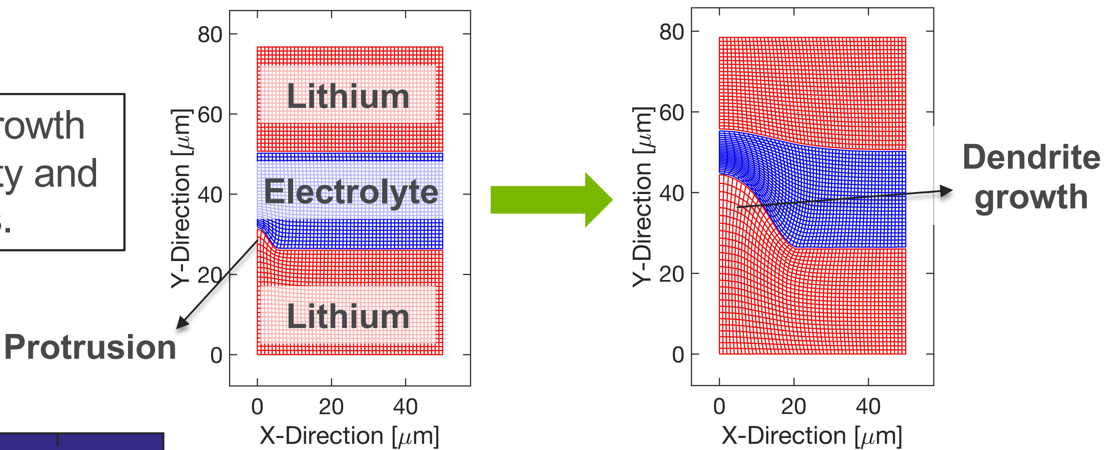
1. How dendrite growth is affected with cycling?

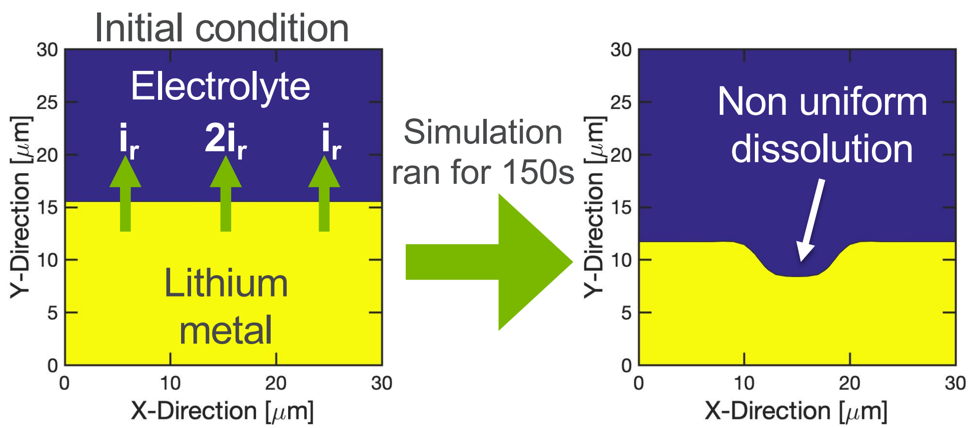
2. What is the impact of lithium dissolution in the dendrite formation/propagation process?

3. Can a coating layer provide a means of promoting adhesion between the cathode and the solid state electrolyte?

PROPOSED FUTURE WORK

Development of a dynamic dendrite growth model that considers the current density and mechanical stress induced effects.



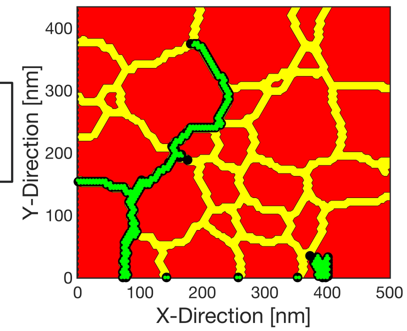


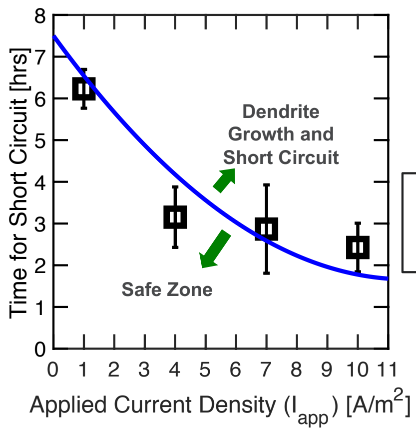
Investigation of lithium dissolution process. (with Jurgen Janek)

Incorporation of cathode-electrolyte interphase (CEI) or interphase protective layers in between cathode and solid-electrolytes.

SUMMARY

Lithium dendrite growth through LLZO microstructure is successfully captured.





Phase map between applied current density and time of deposition have been generated that indicates where short circuit should happen, and which operating conditions are safe.

Delamination induced capacity fade between cathode and LLZO have been captured, which can be minimized by using smaller LLZO grain sizes and limited potential window of operation.